

**United States Patent Application for:**

**MAINTENANCE OF PHOTORESIST ADHESION AND  
ACTIVITY ON THE SURFACE OF DIELECTRIC ARCS FOR  
90 nm FEATURE SIZES**

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1 [0001] **MAINTENANCE OF PHOTORESIST ADHESION AND ACTIVITY ON**  
2 **THE SURFACE OF DIELECTRIC ARCS FOR 90 nm FEATURE SIZES**

3 [0002] **BACKGROUND OF THE INVENTION**

4 [0003] 1. Field of the Invention

5 [0004] The present invention relates to the fabrication of semiconductor devices  
6 having feature sizes in the range of 90 nm and smaller. In particular, the invention relates  
7 to a method of maintaining the adhesion of a photoresist to a surface during development  
8 of a pattern in the photoresist and to maintenance of the functionality of a chemically  
9 amplified photoresist on the surface of a dielectric anti-reflection coating (DARC).

10 [0005] 2. Description of the Background Art

11 [0006] As semiconductor devices are becoming ever smaller, the device features  
12 necessarily become smaller. To produce feature sizes in the range of about 124 nm, for  
13 example, a chemically amplified photoresist (CAR) is pattern imaged using a DUV  
14 wavelength in the range of about 248 nm. To produce the next generation of feature  
15 sizes, in the range of 90 nm, the CAR will be pattern imaged using a radiation wavelength  
16 in the range of about 193 - 198 nm. The chemically amplified photoresists are typically  
17 deposited over the surface of a DARC which reduces reflection during pattern radiation  
18 imaging of the CAR. The composition of the DARC is determined by the refractive index  
19 and extinction coefficient required to attenuate the radiation reflected off the surface of  
20 the device substrate which underlies the DARC.

21 [0007] The DARC used in combination with the CAR deep UV (DUV) photoresists  
22 are frequently deposited by plasma enhanced chemical vapor deposition (PECVD). A  
23 number of techniques have been described for deposition of PECVD films. In general,  
24 the deposition techniques are closely tied to the apparatus used for the deposition,  
25 although some parameters such as process chamber pressure, substrate temperature and  
26 composition of the source gas used to provide the reactive species are relatively

1 independent of the apparatus peculiarities.

2 [0008] In an article entitled "Dual Microwave -- R.F. Plasma Deposition Of  
3 Functional Coatings" by J.E. Klemberg-Sapieha et al. in Thin Solid Films, 193/194  
4 (1990) 965-972, the authors described the deposition of plasma silicon nitride (P-SiN)  
5 and amorphous hydrogenated silicon (a-Si:H) films using a dual-frequency plasma. The  
6 power source for the plasma consisted of a microwave discharge with RF power  
7 simultaneously superimposed on the substrate holder. The negative substrate bias voltage  
8 was said to substantially affect the deposition rate, the film composition, and the film  
9 electrical properties. The authors report that ionic species are estimated to contribute  
10 about 30 % to 40 % to the film growth rate. The increasing ion flux and energy with  
11 increasing substrate bias voltage is said to enhance the formation of densely packed  
12 coatings. As a result, the dielectric loss  $\tan \delta$  of P-SiN, and the resistivity of a-Si:H is said  
13 to be reduced by several orders of magnitude when the substrate bias voltage is raised  
14 from 0 to -800V. The depositions were carried out in a large volume microwave plasma  
15 (LMP®) apparatus of the kind available from AIXTRON AG and Fraunhofer IAF,  
16 Freiburg, Germany, with a MW power at 2.45 GHz applied through a fused silica  
17 window from a periodic slow wave structure. The substrate bias was applied at a  
18 frequency of 13.56 MHz to a powered electrode which functioned as the substrate holder.

19 [0009] A. Raveh et al. discuss the "Deposition and properties of diamond like carbon  
20 films produced in microwave and radio-frequency plasma" in an article in J. Vac. Sci.  
21 Technol. A 10(4), Jul/Aug 1992. In that article the authors report that hard a-C : H films  
22 were grown in a dual frequency plasma sustained simultaneously by microwave and  
23 radio-frequency power. Optimum growth conditions, namely those leading to the most  
24 pronounced  $sp^3$  structural features in the films, are said to depend very strongly on the  
25 methane feed gas flow rate and on the argon concentration in the case of  $CH_4/Ar$  feed gas  
26 mixtures. The optimum conditions are reported to be found to correspond to the  
27 maximum values of ion flux at the growing film surface in combination with high

1 concentrations of precursor species such as CH, C<sub>2</sub>, C<sub>3</sub>, and atomic hydrogen in the  
2 plasma, as revealed by optical emission spectroscopy. Films grown under optimum  
3 conditions are said to have very high microhardness (~50 GPa), high density (1.8 g/cm<sup>3</sup>),  
4 and low internal stress (0.5 GPa). Addition of argon to the methane in the feed gas is  
5 indicated as enhancing the gas phase fragmentation and raising microhardness, but argon  
6 atoms trapped in the film structure increased internal stress. The apparatus which was  
7 used to produce the films was the same apparatus as described above.

8 [0010] International Application No. PCT/US00/20383, of Gill Yong Lee, published  
9 February 8, 2001, discloses the use of a silicon-rich layer over the surface of a dielectric  
10 ARC to prevent "resist poisoning". In particular, the DARC described is an inorganic  
11 ARC layer such as silicon nitride (Si<sub>x</sub>N<sub>y</sub>) or silicon oxynitride (SiN<sub>x</sub>O<sub>y</sub>), or hydrogenated  
12 silicon oxynitride. The DARC is said to be particularly useful during pattern imaging of  
13 the photoresist, typically a CAR which relies on an acid formed in irradiated areas to  
14 enable development of the pattern. However, the presence of amine radicles which are  
15 contributed by the DARC contaminates the CAR applied over the DARC, neutralizing  
16 the acid-generators. This makes the contaminated portions of the resist insoluble by the  
17 developer. As a result, a "foot" is present at the base of the developed resist profile. To  
18 prevent this problem, a capping layer is applied over the DARC prior to application of the  
19 CAR. In one embodiment, the capping layer is silicon, preferably a thin amorphous  
20 silicon layer. The silicon layer is said to be sufficiently thin to avoid causing standing  
21 waves and interference in the resist. Alternatively, the cap layer may be a mono-atomic  
22 layer that alters the surface morphology of the DARC. The mono-atomic layer, in one  
23 embodiment comprises excess silicon dangling bonds on the surface of the DARC. For  
24 example, the cap layer could comprise a silicon-rich oxide or a silicon-rich oxynitride if  
25 the DARC comprised silicon oxide or an oxynitride layer.

26 [0011] U.S. Patent No. 6,227,141 of Sharan et al., issued May 8, 2001, describes an  
27 RF powered, plasma enhanced chemical vapor deposition reactor and methods of use of

1 the reactor. The plasma enhanced chemical vapor deposition (PECVD) apparatus makes  
2 use of a first RF power source which delivers RF power at a first frequency to a first  
3 electrode, and a second RF power source which delivers RF power at a second frequency  
4 to a second electrode.

5 [0012] Applied Materials, Inc., Santa Clara, California offers both single and dual  
6 frequency PECVD chambers. The multifrequency processing chambers typically apply  
7 two different RF power frequencies to a single electrode.

8 [0013] U.S. Patent No. 6,171,764 to Ku et al., issued January 9, 2001 describes the  
9 kinds of radiation reflection problems which may occur in photolithographic processes.  
10 The description relates to semiconductor manufacturing processes which make use of a  
11 dielectric anti-reflective (DARC) layer to reduce reflected radiation during photoresist  
12 imaging. In particular, the difference between the Ku et al. invention and other known  
13 methods is based on the ordering of specific layers in the substrate used in the  
14 photolithographic process. In the Ku et al. method, the DARC layer is applied over a  
15 substrate, followed by a hard mask layer, and then a photoresist. This is said to compare  
16 with other known methods where the DARC layer is used between the photoresist layer  
17 and the hard mask layer. (Col. 3, lines 35 - 46.)

18 [0014] U.S. Patent No. 6,607,984 to Lee et al., issued August 19, 2003 describes a  
19 method of semiconductor fabrication in which an inorganic anti-reflection coating is  
20 employed and subsequently removed by selective etching relative to an underlying  
21 inorganic dielectric layer. (Col. 1, lines 61 - 67, continuing at Col. 2 lines 1 - 6.)

22 [0015] European Patent Application No. 99204265.5 of Shao -Wen Hsia et al.,  
23 published June 21, 2000, describes a semiconductor interconnect structure employing an  
24 inorganic dielectric layer produced by plasma enhanced chemical vapor deposition  
25 (pecvd). In accordance with a preferred embodiment of the invention, a metal layer upon  
26 which photoresist patterns are developed comprises a sandwiched metal stack having a  
27 layer of conducting metal (aluminum, titanium, and the like) bounded by an upper thin-

1 film ARC layer and a bottom thin-film barrier layer, where at least the top layer is  
2 composed of an inorganic dielectric substance. The use of an inorganic dielectric top  
3 ARC layer is said to facilitate the use of thinner photoresist layers while preserving the  
4 integrity of the photoresist pattern for deep sub-micron feature sizes. (Col. 1, lines 56 -  
5 58, continuing at Col. 2, lines 1 - 8.)

6 [0016] We have encountered a problem which does not appear to be addressed in the  
7 known art, but which has become important in particular with respect to semiconductor  
8 substrate features in the 90 nm range and smaller. During development of the  
9 photoresist, applicants have encountered instances where the photoresist becomes  
10 detached from the underlying substrate. Development refers to treatment of the  
11 photoresist with a fluid, typically a liquid reagent, to remove portions of the photoresist,  
12 thus creating a pattern. For reference purposes, when the portions of the photoresist  
13 which are removed are the portions which have been exposed to patterning radiation, the  
14 photoresist is said to be a positive photoresist. When the portions of the photoresist  
15 which are removed are the portions which have not been exposed to patterning radiation,  
16 the photoresist is said to be a negative photoresist.

17 [0017] In addition to detachment of areas of the photoresist from the underlying  
18 substrate, we have continued to observe reaction at the interface between an underlying  
19 DARC and the photoresist. This reaction is despite the use of a nitrogen-free DARC. It  
20 is possible to use a capping layer of the kind described in the art to isolate the photoresist  
21 from an underlying DARC. However, typically the semiconductor manufacturing  
22 process is a dual damascene process, which is common in multilevel metal devices. In a  
23 dual damascene process, after the first photoresist patterning process, there is an etch  
24 through underlying layers, including the DARC using the photoresist as a pattern.  
25 Subsequently, the portions of the opened pattern are filled with a buried ARC (BARC),  
26 followed by application of a second layer of photoresist and creation of a second pattern  
27 in the photoresist. Typically the second layer of photoresist is in contact with the DARC

1 at the surface area where the etch passed through the DARC. Thus, there are still  
2 significant photoresist “poisoning” problems even when a capping layer is applied over  
3 the upper surface of the DARC as a part of the preparation for the first patterning step.

4 [0018] A need exists for ensuring photoresist adhesion and uniform lithographic  
5 imaging and development activity on the surface of various underlying substrates  
6 (particularly on the surface of dielectric arcs) during the fabrication of semiconductor  
7 devices with feature sizes of 90 nm and smaller.

8 [0019] **SUMMARY OF THE INVENTION**

9 [0020] We have traced the detachment of photoresist during development of patterned  
10 features in the range of about 90 nm and smaller to a combination of the reduced “foot  
11 print” of the pattern on the underlying substrate and to the contact angle between the  
12 underlying substrate surface and the developing reagent used to develop a pattern in the  
13 photoresist. We have determined that by maintaining a contact angle of about 20 degrees  
14 or greater, and preferably 35 degrees or greater, the detachment of the photoresist from  
15 the underlying substrate can be avoided for photoresists including feature sizes in the  
16 range of about 90 nm. As feature sizes grow even smaller, it may be necessary to  
17 continually increase the contact angle to maintain adhesion of the photoresist to the  
18 underlying substrate during development of the photoresist. The key is to reduce the  
19 force exerted against the photoresist wall as the feature size becomes smaller, with the  
20 concurrent reduction in foot print of the photoresist on the underlying substrate surface.

21 [0021] The contact or wetting angle of the substrate depends on the composition of  
22 both the substrate and the developer used for photoresist development. The embodiments  
23 described below pertain to a DARC, and in particular a DARC comprised of  $\text{SiO}_x\text{H}_y : \text{C}$ ,  
24 where x ranges from greater than 1 to about 2.0, and H ranges from about 0.1 to about  
25 0.3, and the carbon content ranges from 0 % up to 5.0% (typically less than about 3.0%).  
26 The reagents used to produce the DARC by PECVD are typically  $\text{SiH}_4$ , and  $\text{CO}_2$ , with

1 helium added as a diluent plasma source gas, which also provides species for surface  
2 bombardment of the depositing film. For a silane-based PECVD film deposition  
3 process, where the silicon-containing precursor is  $\text{SiH}_4$ , the carbon content in the  
4 polymeric film structure is typically less than about 3 %, which is contributed by  $\text{CO}_2$   
5 used in the film formation process. We have discovered that an increase in carbon  
6 content of the DARC produces a higher contact angle, which is beneficial in terms of  
7 reducing the potential for detachment of the photoresist from the DARC surface during  
8 development of the photoresist using a water based developer of the kind commonly used  
9 in the semiconductor industry. To achieve a higher carbon content in the DARC, the  
10 amount of  $\text{CO}_2$  used in the  $\text{SiH}_4$  / $\text{CO}_2$  process may be increased to some extent; in an  
11 alternative, the silane-based precursor used in the PECVD deposition of the DARC may  
12 contain carbon, such as trimethyl silane  $((\text{CH}_3)_3\text{HSi})$  or tetramethyl silane  $((\text{CH}_3)_4\text{Si})$ , for  
13 example, but not by way of limitation.

14 [0022] Other Group IV elements such as silicon, germanium, tin and lead, by way of  
15 example and not by way of limitation, which are present in the DARC film may be  
16 increased in concentration, in a manner similar to the carbon content, to increase the  
17 contact angle between the DARC surface and the fluid photoresist developer.

18 [0023] While an increased carbon content in the DARC increases the contact angle  
19 and has a beneficial effect in terms of reducing photoresist detachment from the DARC  
20 surface during development, a higher carbon content in a silane precursor for PECVD  
21 film formation is generally more expensive and carbon particulate byproducts of the film  
22 deposition may require more frequent deposition process chamber cleaning. The  
23 improved attachment of the photoresist during development may justify the increased  
24 chamber maintenance costs in terms of throughput in some instances. As an alternative,  
25 it is possible to use a lower carbon content DARC, but to use a surface treatment of the  
26 DARC to increase the contact angle with the developer; or to use a developer which  
27 provides a higher contact angle on the DARC surface.



1 [0024] We have achieved an increased contact angle between the DARC surface  
2 and a water-based, basic CAR photoresist developer by treating the surface of the DARC  
3 after formation of the DARC film. In particular, the DARC film surface has been treated  
4 with a hydrogen plasma or a helium plasma to provide an increase in the contact angle.  
5 Preferably, the hydrogen plasma is used for the DARC film surface treatment, as this  
6 process provides a greater shelf life for the DARC coated substrate prior to subsequent  
7 use and provides very good uniformity of performance across the entire substrate.

8 [0025] The most commonly used DUV photoresists for semiconductor device  
9 manufacture are the positive chemically amplified photoresists (CARs), which rely upon  
10 the generation of an acid in the irradiated portion of the photoresist to form a latent image  
11 which is subsequently developed using a basic developer. The photoresist pattern  
12 developer is commonly a basic, water-based developer. The presence of a base on the  
13 surface of a DARC at the time the CAR is applied causes subsequent problems in pattern  
14 production, because the acid generated in the CAR upon irradiation reacts with the base  
15 on the surface of the DARC, producing areas at the interface of the DARC and the CAR  
16 which do not contain the acid generated by the irradiation. Development of the  
17 photoresist pattern at this interfacial area does not occur properly when the basic  
18 developing agent is applied to the photoresist. We have discovered that it is not enough  
19 to remove nitrogen-containing species from the surface of the DARC. It is also necessary  
20 to reduce the presence of OH groups from the surface of the DARC. The treatment of the  
21 DARC surface with a hydrogen plasma prior to photoresist application to the DARC  
22 surface not only increases the contact angle between the DARC and a water-based  
23 photoresist developer, it also reduces the available OH groups on the surface of the  
24 DARC, reducing photoresist poisoning during deposition, and pattern latent image  
25 formation of the photoresist. Treatment of the DARC surface with helium prior to  
26 photoresist application also tends to reduce the available OH groups on the surface of the  
27 DARC, but has a limited performance time window, and has been less uniform in ability

to reduce photoresist poisoning under currently known treatment conditions.

**[0026] BRIEF DESCRIPTION OF THE DRAWINGS**

[0027] Figure 1 A shows a diagram 100 of a liquid droplet 102 in contact with a substrate 103, where the contact angle 104, referred to as  $\alpha_1$ , in the range of about 18 degrees.

[0028] Figure 1B shows a diagram 100 of a liquid droplet 106 in contact with a substrate 103, where the contact angle 108, referred to as  $\alpha_2$ , is in an acceptable range, about 70 degrees, for the present invention.

[0029] Figure 1C shows a diagram 100 of a liquid droplet 110 in contact with a substrate 103, where the contact angle 112, referred to as  $\alpha_3$ , is in an acceptable range, about 155 degrees, for the present invention

[0030] Figure 2A shows a schematic top view 200 of an SEM image for a developed CAR on the surface of a  $\text{SiO}_x\text{N}_y$  DARC, where the contact angle between the DARC and the developer for the photoresist was about 5.1 degrees.

[0031] Figure 2B shows a schematic top view 210 of an SEM image for a developed CAR on the surface of a  $\text{SiO}_x\text{H}_y$  DARC, where the contact angle between the DARC and the developer for the photoresist was about 3.7 degrees.

[0032] Figure 2C shows a schematic top view 220 of an SEM image for a developed CAR on the surface of a  $\text{SiO}_x\text{H}_y$  DARC, where the contact angle between the DARC and the developer for the photoresist was about 34.5 degrees.

1 [0033] Figure 2D shows a schematic top view 230 of an SEM image for a developed  
2 CAR on the surface of a hydrogen plasma treated  $\text{SiO}_x\text{H}_y$  DARC, where the contact angle  
3 between the DARC and the developer for the photoresist was about 63 degrees.

4 [0034] Figure 2E shows a schematic top view 240 of an SEM image for a developed  
5 CAR on the surface of a silicon-rich, nitrogen- free DARC, where the contact angle  
6 between the DARC and the developer for the photoresist was about 3.5 degrees.

7 [0035] Figure 3 is a graph showing the change in contact angle between a nitrogen-  
8 free DARC 193,  $\text{SiO}_x\text{H}_y$  surface and a water-based alkaline photoresist developer, where  
9 the DARC 193 surface was treated with a helium plasma. Initially, the contact angle  
10 between the DARC surface and the developer was about 30 degrees to about 40 degrees  
11 depending on the plasma treatment time. The contact angle change is shown as a function  
12 of passing time in days, where each curve represents a different helium plasma treatment  
13 period.

14 [0036] Figure 4 is a graph showing the change in contact angle between a nitrogen-  
15 free DARC 193,  $\text{SiO}_x\text{H}_y$  surface and HMDS photoresist developer, where the DARC 193  
16 surface was treated with a hydrogen plasma. Initially, the contact angle between the  
17 DARC surface and the developer was about 60 degrees. The contact angle change is  
18 shown as a function of passing time in days, where each curve represents a different  
19 hydrogen plasma treatment period.

20 [0037] Figure 5 is a graph 500 showing the compressive stress on scale 504 of a  
21 nitrogen-free DARC 193 film of varying atomic composition, as a function of the process  
22 conditions on scale 502, where single frequency (SF) plasma deposition was used in some  
23 instances and multiple frequency (MF) plasma deposition was used in other instances. In

1 addition, in some instances the inert gas in the plasma source gas was argon (AR), while  
2 in some other instances the inert gas was helium (He).

3 [0038] Figure 6 is a graph 600 showing reduction in extinction coefficient,  $k$ , after  
4  $O_2$  ashing for photoresist removal, on scale 604, of a nitrogen-free DARC 193 film, where  
5 films of varying nitrogen composition were evaluated, as a function of the process  
6 conditions on scale 602, where single frequency (SF) plasma deposition was used in some  
7 instances and multiple frequency (MF) plasma deposition was used in other instances. In  
8 addition, in some instances the inert gas in the plasma source gas was argon (AR), while  
9 in some other instances the inert gas was helium (He).

10 [0039] Figure 7 is a graph 700 showing change in extinction coefficient,  $k$ , after 9  
11 days of storage at room temperature in ambient atmosphere of a clean room, on scale 704,  
12 of a nitrogen-free DARC 193 film, where films of varying nitrogen composition were  
13 evaluated, as a function of the process conditions on scale 702, where single frequency  
14 (SF) plasma deposition was used in some instances and multiple frequency (MF) plasma  
15 deposition was used in other instances. In addition, in some instances the inert gas in the  
16 plasma source gas was argon (AR), while in some other instances the inert gas was  
17 helium (He).

18 [0040] Figure 8 is a graph 800 showing the post oxygen plasma ashing reduction in  
19 refractive index ( $n$ ) on scale 802, for a nitrogen-free DARC 193 film, as a function of the  
20 compressive stress of the DARC film on scale 804. Curve 806 represents a DARC film  
21 having an extinction coefficient ( $k$ ) of 0.35; Curve 808 represents a DARC film having a  
22  $k$  of 0.6; and Curve 810 represents a DARC film having a  $k$  of 0.95. The extinction  
23 coefficient is a function of the chemical composition of the film. The thickness of each  
24 film was about 250 Å.

1  
2 [0041] Figure 9 is a graph 900 showing the post oxygen ashing reduction in  
3 extinction coefficient (k) on scale 902, for a nitrogen-free DARC 193 film, as a function  
4 of the compressive stress of the DARC film on scale 904. Curve 906 represents a DARC  
5 film having an initial extinction coefficient (k) of 0.35; Curve 908 represents a DARC  
6 film having an initial k of 0.6; and Curve 910 represents a DARC film having an initial k  
7 of 0.95. The thickness of each film was about 250 Å.

8 [0042] **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS**

9 [0043] As a preface to the detailed description, it should be noted that, as used in this  
10 specification and the appended claims, the singular forms "a", "an", and "the" include  
11 plural referents, unless the context clearly dictates otherwise.

12 [0044] As mentioned above, we have traced the detachment of photoresist during  
13 development of patterned features in the range of about 90 nm and smaller to a  
14 combination of the reduced "foot print" of the pattern on the underlying substrate and to  
15 the contact angle between the underlying substrate surface and the developing reagent.  
16 We have determined that by maintaining a contact angle of about 20 degrees or greater,  
17 preferably 35 degrees or greater, the detachment of the photoresist from the underlying  
18 substrate can be avoided for photoresists including feature sizes in the range of about 90  
19 nm or smaller.

20 [0045] Figure 1A is a simple diagram showing a top view of a substrate surface 103  
21 with a liquid droplet 102 on the surface 103. The contact angle between the surface 103  
22 and droplet 102 is the angle between the horizontal substrate surface and a tangent drawn  
23 along the curvature of the droplet 102 at the edge of droplet 102. The contact angle can  
24 approach zero degrees when the droplet 102 wets surface 103 well and the tangent line is  
25 nearly flat. In Figure 1A, the contact angle 102, referenced as  $\alpha_1$ , is illustrated as being  
26 about 18 degrees. This contact angle is just slightly below the minimum contact angle we

1 have determined to be adequate to protect a photoresist having 90 nm feature sizes against  
2 detachment from an underlying surface during development of a latent irradiated image in  
3 the photoresist (into a patterning mask having the 90 nm features).

4 [0046] Figure 1B shows another droplet 106 of a material which forms a contact  
5 angle 108, referenced as  $\alpha_2$ , with substrate 103. The contact angle in Figure 1B is  
6 illustrated as being about 70 degrees, well above the minimum contact angle of about 20  
7 degrees which is recommended to prevent photoresist detachment for 90 nm photoresist  
8 features.

9 [0047] The basic concept of the present invention with respect to the affect of contact  
10 angle on adhesion of photoresist to an underlying substrate during development of the  
11 photoresist is applicable to any underlying substrate and the developing fluid used to  
12 develop the photoresist. For purposes of illustration, the experimental embodiments  
13 described were carried out using DARC® (Applied Materials, Inc.) 193 substrates. In  
14 some instances, the surfaces of the DARC® 193 substrate was surface treated prior to  
15 application of the photoresist. The initial adhesion studies were carried out on DARC®  
16 193 substrates where the photoresist applied over the substrate and developed into a  
17 pattern was a developer used during the initial adhesion study was a SHIPLEY® UV6  
18 (248 nm) CAR. The developer used to develop the UV6 CAR was a  
19 tetramethylammonium hydroxide (TMAH)-containing aqueous alkaline solution, with the  
20 specific formulation being that recommended by Shipley Company, Marlborough,  
21 Massachusetts, for developing the Shipley UV6 CAR. Subsequent to the initial studies,  
22 additional experimentation has been carried out in which a JSR AT237 CAR (193 nm)  
23 photoresist was used for purposes of evaluating the effect of photoresist adhesion and  
24 poisoning effects with respect to 90 nm pattern feature sizes.

25 [0048] The initial adhesion studies, which used the SHIPLEY® UV 6 photoresist  
26 employed a photoresist thickness in the range of about 3,000 Å to about 4,000 Å. The

1 patterning of the photoresist was carried out using a CANON® FPA-5000ES2 exposure  
2 tool which provided 248 nm radiation. The target feature was a 100nm line/120nm space.  
3 The reticle was a SCAA mask. An HMDS treatment was carried out on the DARC  
4 substrate for 30 seconds prior to photoresist application. The development of the  
5 photoresist was carried out for 60 seconds under conditions recommended for the  
6 SHIPLEY® UV6 photoresist.

7 [0049] A typical experimental substrate included, from bottom to top, a silicon  
8 substrate; a 600 Å thick layer of  $\alpha$ -carbon; a 250 Å thick layer of DARC or DARC 193; a  
9 treated surface on the DARC or DARC 193, or a capping layer over the DARC or DARC  
10 193 surface; and an approximately 3,200 Å thick layer of the Shipley UV 6 CAR.

11 [0050] The DARC and DARC 193 anti-reflective coatings which were used in the  
12 experimental embodiments were applied using PECVD in an Applied Materials, Inc.  
13 PRODUCER® system in a twin PECVD processing chamber. Applied Materials, Inc.  
14 has offices in Santa Clara, California. The comparative example DARC film was a  
15 standard  $\text{SiO}_x\text{N}_y$ , where x was approximately 1.25 and y was approximately 0.25.

16 [0051] The DARC 193 was a nitrogen-free  $\text{SiO}_x\text{H}_y\text{:C}$  film, where x ranged from  
17 greater than 1 to about 2.0, and y ranged from about 0.1 to about 0.3, with a carbon  
18 content ranging from about 0 % to 5 %, and typically in the range of about 3 %, unless  
19 specified to be different. The precursors used to produce the DARC 193 film were silane  
20 ( $\text{SiH}_4$ ),  $\text{CO}_2$ , and helium. An additional nitrogen-free DARC 193 film was made to  
21 achieve increased carbon content in the film, where the precursor silane was trimethyl  
22 silane ( $\text{CH}_3$ )<sub>3</sub>HSi. However, one skilled in the art will understand that other carbon-  
23 containing silanes could be substituted as precursor materials for deposition of the DARC  
24 by PECVD techniques known in the art.

25 [0052] As previously mentioned, although an increased carbon content in the DARC  
26 increases the contact angle and has a beneficial effect in terms of reducing photoresist

1 detachment from the DARC or DARC 193 surface during development, the higher carbon  
2 content silane precursors for PECVD film formation are more expensive and require more  
3 frequent process chamber cleaning. The improved attachment of the photoresist during  
4 development may justify the increased chamber maintenance costs in terms of throughput  
5 in some instances. Other Group IV elements such as (an increased amount of) silicon, or  
6 germanium, or tin, or lead, for example and not by way of limitation, may be incorporated  
7 into a DARC or DARC 193 film to increase the contact angle. One skilled in the art can  
8 determine with minimal experimentation the amount of the Group IV element which must  
9 be included to obtain a contact angle which is adequate, in view of the present disclosure.

10 [0053] As an alternative to inclusion of a Group IV element other than silicon, or to  
11 increasing the silicon content in the DARC or DARC 193 film, it is possible to use a  
12 surface treatment of the DARC to reduce the contact angle with the developer; or to use a  
13 developer which provides a higher contact angle on the DARC surface.

14 [0054] We have achieved an increased contact angle between the DARC surface and  
15 a water-based, alkaline CAR photoresist developer by treating the surface of the DARC  
16 after formation of the DARC. We have demonstrated that treatment of a DARC film after  
17 formation with a hydrogen plasma or a helium plasma increases the contact angle between  
18 the DARC surface and a water-based photoresist developing agent. The hydrogen and  
19 helium plasma treatments of a deposited DARC film were carried out in a PRODUCER®  
20 twin PECVD chamber using a single frequency RF power source for plasma generation.  
21 Preferably, the hydrogen plasma is used for the DARC film surface treatment, as this has  
22 provided a long shelf life for the DARC coated substrate prior to application of a  
23 photoresist and has provided better uniformity of performance across a wafer substrate  
24 compared with a helium treatment, as will be discussed in more detail below.

25 [0055] The DARC 193 film typically used in the example embodiments described  
26 below was deposited in the PRODUCER® twin PECVD chamber of Applied Materials,



1 Inc.

2 [0056] In some instances, the DARC 193 film was prepared using a single 13.56  
3 frequency RF power source. The general process conditions for a  $\text{SiO}_x\text{H}_y$  : C 193 DARC  
4 film deposition using a single frequency power source were:  $\text{SiH}_4$  flow rate of 40 to 80  
5 sccm,  $\text{CO}_2$  flow rate of 900 to 4,000 sccm, He flow rate of 2,000 sccm to 12,000 sccm;  
6 plasma source power 100 W to 175W; spacing between the shower head and the substrate  
7 ranged from 400 mils to 800 mils; the substrate temperature was  $350^\circ\text{C} \pm 50^\circ\text{C}$ ; the  
8 process chamber pressure ranged between 4 Torr and 8 Torr.

9 [0057] In other instances, a multiple frequency, typically a dual frequency RF power  
10 source was used to generate the plasma, where each of the multiple frequency power  
11 applications was made to the same electrode. Table I, below, shows a series of process  
12 conditions and measured values representative of production of the  $\text{SiO}_x\text{H}_y$  : C films in  
13 the PRODUCER® twin PECVD process chamber. The application of dual frequency  
14 power sources during deposition of the DARC 193  $\text{SiO}_x\text{H}_y$  : C films has proved to reduce  
15 photoresist poisoning, increase the shelf life of the DARC 193 coated substrate prior to  
16 photoresist application, and has improved maintenance of refractive index and extinction  
17 coefficient of the DARC 193 film during oxygen plasma ashing for removal of residual  
18 photoresist, as will be discussed in more detail subsequently herein.

[0058]

TABLE I

**MULTIPLE FREQUENCY DARC 193 FILM DEPOSITION PROCESS AND DATA**

SiH <sub>4</sub> (sccm)	CO <sub>2</sub> (slm)	He (slm)	Pressure (Torr)	HF (Watts)	LF (Watts)	Thic k-ness (Å)	n (193nm)	k @ 150Å	k @ 250Å	Stress (Mpa)
40	2.5	5	5.5	65	20	152	1.8098	0.2292	0.2914	-163
40	2.5	5	5.5	65	20	151	1.8084	0.2281	0.2960	
40	1.8	6	5.5	65	15	156	1.7736	0.2958	0.3686	-154
40	1.8	6	5.5	65	15	156	1.7762	0.2943	0.3718	
40	2.5	6	5.5	65	20	149	1.8216	0.1992	0.2720	-172
40	2.5	6	5.5	65	20	148	1.8082	0.2101	0.2813	
40	2.5	6	4.8	65	15	147	1.8103	0.2015	0.2762	-156
40	2.5	6	4.8	65	15	146	1.7849	0.2169	0.2777	
40	3.0	6	5.5	65	20	148	1.8065	0.1846		
40	3.5	6	5.5	65	20	141	1.8433	0.1297		
40	4.0	6	5.5	65	20	140	1.8061	0.1132		

[0059] The substrate temperature for all of the film preparation was  $350 \pm 50^\circ\text{C}$ . The HF (high frequency) power was at 13.56 MHz; the LF (low frequency) power was at 350 kHz. The spacing between the shower head and the substrate was approximately 500 mils. The film deposition time was 8.5 seconds; and the deposition rate ranged from about 990 to about 1075 Å per minute. The symbol “n” represents refractive index, and the symbol “k” represents the extinction coefficient. Sccm refers to standard cc per minute; slm refers to standard liters per minute. The reference to 150 Å and 250 Å with respect to the k value indicates the thickness of the DARC.193.

[0060] The nitrogen-free (N-free) dielectric anti-reflective coating SiO<sub>x</sub>H<sub>y</sub>:C was developed to reduce the poisoning interaction caused when NO<sub>2</sub> is used as a precursor during deposition of the DARC 193. However, we learned, after considerable testing, that the presence of -OH radicals, which either exist inherently in the DARC or result from H<sub>2</sub>O absorption on the DARC surface also cause photoresist poisoning of a CAR

1 positive photoresist. Current investigation has revealed that poisoning can be eliminated  
2 by surface acidification of the DARC after deposition. The DARC surface acidification  
3 circumvents the neutralization of photo-generated  $H^+$  in the CAR by the  $-OH$  radicals  
4 inherently in the DARC. In addition, we have discovered that a more dense ARC film  
5 makes it difficult for  $-OH$  radicals to form on the DARC surface due to  $H_2O$  absorption.  
6 Compressive film stress is an indication of film density, and directly correlates to  
7 resistance to  $H_2O$  absorption on the DARC film surface.

8 [0061] It was possible to greatly improve the DARC resistance to  $H_2O$  absorption by  
9 creating and maintaining a deposition process regime that makes the DARC film more  
10 dense. This dense DARC film with an acidified surface has demonstrated promising  
11 lithography performance with minimal resist poisoning, as well as excellent shelf life and  
12  $O_2$  ashing resistance. Combination of DARC film densification, DARC film surface  
13 acidification, and a DARC film surface which provides a high contact angle during  
14 development of the photoresist ensures both excellent pattern development and adhesion  
15 of the photoresist during development for 193 nm lithography, and during the patterning  
16 of 90 nm and smaller features.

17 [0062] For reference purposes, a PECVD nitrogen-containing DARC typically has a  
18 composition  $SiO_xN_yH_z$ , where Si is typically about 55 atomic percent, O is about 35  
19 atomic percent and N is about 15 % or less of the DARC composition. The new N-free  
20 DARC 193 composition  $SiO_xH_y : C$  is such that Si ranges from about 40 atomic % to 45  
21 atomic %, O ranges from about 40 atomic % to 51 atomic %, H ranges from about 4  
22 atomic % to about 15 atomic %, and C ranges from about 0 atomic % to about atomic  
23 5%, but is typically less than about 3 atomic %. The DARC 193 is produced by PECVD  
24 using  $SiH_4$ , an oxygen source, and an inert gas as precursors. When the oxygen source is  
25  $CO_2$ , this contributes carbon to the DARC 193 film.

26 [0063] When the silane used as a precursor contains carbon, such as a trimethyl or  
27 tetramethyl silane, for example, the DARC 193 film contains Si ranging from about 20

1 atomic % to 50 atomic %, O ranges from about 10 atomic % to about 20 atomic %, H  
2 ranges from about 10 atomic % to about 50 atomic %, and C ranges from about 10 atomic  
3 % to about 50 atomic %.

4 [0064] When photoresist poisoning occurs, electron pairs from a basic group attract  
5 protons from the 193 nm positive-acting chemically-amplified photoresist, neutralizing  
6 the formation of an acid in irradiated areas of the photoresist, typically at the interface of  
7 the photoresist adjacent the DARC surface. The poisoning manifests itself as a bump in  
8 via structures, footing, scums, and a rough surface on a substrate.

9 [0065] We determined that use of multiple frequency power application during  
10 deposition of a DARC increases the density of the DARC film, as previously mentioned;  
11 this improves the film resistance to H<sub>2</sub>O absorption. As a result, the shelf life of the  
12 deposited DARC film and the maintenance of refractive index and extinction coefficient  
13 of the DARC film is improved with the use of multiple, typically dual, frequency power  
14 application during the deposition of the DARC film. By using optical measurements and  
15 FTIR, we were able to correlate film stress, which is an indicator of film density, with the  
16 increased shelf life and maintenance of refractive index and extinction coefficient for a  
17 variety of different film compositions. The detailed data is presented in the embodiment  
18 examples provided below.

19 [0066] However, the DARC films deposited under process conditions which  
20 produce a dense film, such as a plasma source gas flow rate of SiH<sub>4</sub> at 40 sccm, CO<sub>2</sub> at  
21 2.5 slm, and He at 6 slm; at a pressure of 5.5 Torr, with 65 W of HF power and 20 W of  
22 LF power, for example, and not by way of limitation, exhibit a contact angle in the range  
23 of about 5 degrees. Although the photoresist poisoning problem may be avoided by the  
24 dense film, when the patterned feature size of the photoresist is 120 nm or smaller, and  
25 particularly 90 nm and smaller, this contact angle is not adequate to ensure that the  
26 photoresist will remain attached to the DARC film surface during development of the  
27 photoresist pattern.

1 [0067] As discussed above, when the composition of a DARC 193 ( $\text{SiO}_x\text{H}_y$  : C) film  
2 does not provide an adequate contact angle, or when the developed pattern is poor, it is  
3 possible to increase the contact angle and to reduce resist poisoning by treating the  
4 surface of the DARC 193 film after deposition. We have treated various DARC 193 film  
5 surfaces with plasmas of  $\text{CO}_2$ ,  $\text{H}_2$ , and He. We have also placed a capping layer of  $\alpha$ -  
6 silicon on the DARC 193 film surface. The results achieved using these surface  
7 treatment techniques are illustrated in Figures 2A through 2E. The DARC 193 films  
8 which were treated were prepared using dual frequency RF power application of the kind  
9 described above.

10 [0068] EXAMPLE EMBODIMENTS

11 [0069] Example One:

12 [0070] As a comparative example, a SiON DARC having an n (refractive index) of  
13 1.9 and a k (extinction coefficient) of 0.3 @ 248 nm was capped with a 50 Å thick silicon  
14 oxide capping film generated from a  $\text{SiH}_4$  / $\text{CO}_2$ / helium plasma using the general PECVD  
15 conditions of the kind described above for a single frequency plasma deposition process.  
16 The capped DARC exhibited a contact angle of 5.1 degrees with the water based alkaline  
17 developer used to develop the CAR, which was the SHIPLEY® UV6 photoresist. After  
18 exposure to either 230 J or 280 J of 248 nm patterning radiation, followed by  
19 development of the pattern, a photomicrograph of a top view 200 of the developed  
20 photoresist had the appearance illustrated by the schematic shown in Figure 2A. The  
21 oxide-capped SiON DARC surface 202 was completely exposed in patterned areas after  
22 development of the photoresist, because the lines and spaces pattern which was to be  
23 developed failed due to detachment of the photoresist during development in areas 204.

24 [0071] Example Two:

25 [0072] As a second comparative example, a nitrogen-free DARC 193  $\text{SiO}_x\text{H}_y$  : C  
26 film having an n of 1.9 and a k of 0.3 @ 248 nm, which was surface treated with a  $\text{CO}_2$   
27 plasma for a time period of about 20 seconds, using a  $\text{CO}_2$  flow rate of about 3slm in a 200

1 mm PRODUCER® twin PECVD process chamber, using the single frequency plasma  
2 deposition process. The pressure was about 5 Torr, at a substrate temperature of about  
3 350 °C, at a plasma source power of about 50 - 100 W at 13.56 MHz, and at a shower head  
4 spacing of 450 mils from the substrate surface. The CO<sub>2</sub>-treated DARC 193, exhibited a  
5 contact angle of only 3.5 degrees with respect to the photoresist water-based alkaline  
6 developer. Exposure of the CAR to either 230 J or 280 J of 248 nm patterning radiation,  
7 and development of the imaged photoresist resulted in a developed photoresist where none  
8 of the patterned areas were present. All of the developed feature areas became detached  
9 from the DARC surface and washed away on development.

10 [0073] Example Three:

11 [0074] As a third comparative example, a nitrogen-free DARC 193 SiO<sub>x</sub>H<sub>y</sub> : C film  
12 having an n of 1.9 and a k of 0.3 @ 248 nm, which was not surface treated, exhibited a  
13 contact angle of about 3.7 degrees with respect to the same developer mentioned with  
14 respect to Example Two. Exposure of the SHIPLEY® UV6 photoresist to 230 J of 248  
15 nm patterning radiation, followed by development of the latent irradiated image in the  
16 photoresist, produced a relatively acceptable pattern. However, exposure of the CAR to  
17 280 J of 248 nm patterning radiation, followed by development, produced a defective  
18 pattern in the CAR of the kind illustrated in Figure 2B. Figure 2B is a schematic top view  
19 210 of a photomicrograph of the patterned photoresist. The DARC 193 surface 212 was  
20 exposed in some areas where the photoresist 216 should have been present. The  
21 photoresist 216 became detached, leaving broken off areas 214 where photoresist was  
22 missing. The difference in the developed pattern with such a slight difference in the  
23 amount of energy applied during radiation of the pattern indicates that the combination of  
24 the imaging and development process is not reliable for manufacturing purposes. We  
25 needed to provide an imaging and development process which was sufficiently reliable for  
26 production.

27 [0075] Example Four:

1 [0076] In a first example of the invention, a DARC 193  $\text{SiO}_x\text{H}_y$  : C film having an n  
2 of 1.9 and a k of 0.3 @ 248 nm, which was surface treated with a single frequency-  
3 generated hydrogen plasma for a time period of about 10 seconds, using a hydrogen flow  
4 rate of 600 sccm in the 200 mm PRODUCER® twin PECVD process chamber, at a  
5 pressure of ranging from about 2 Torr to about 10 Torr (typically about 5.5 Torr), at a  
6 substrate temperature of about  $350 \pm 50$  °C, at a plasma source power of 300W at 13.56  
7 MHz, and at a shower head spacing of 450 mils from the substrate surface, exhibited a  
8 contact angle of about 63 degrees with respect to the same developer mentioned with  
9 respect to Example Three. Exposure of the photoresist to either  $230 \text{ J/m}^2$  or  $280 \text{ J/m}^2$  of  
10 248 nm patterning radiation, followed by development of the image using the developer  
11 produced a very acceptable pattern of approximately 110 nm features in the CAR. The  
12 pattern produced is illustrated in Figure 2D. Figure 2D is a top view 230 of a  
13 photomicrograph of the patterned photoresist. Experimentation has indicated that the  
14 nitrogen-free DARC 193 with the hydrogen surface treatment has a comparable  
15 lithography window with respect to a BARC used for poly gate applications. This is  
16 because the  $\text{H}_2$  treatment does not affect reflectivity as much as a capping layer of  $\alpha$ -  
17 silicon, for example.

18 [0077] Example Five:

19 [0078] In a second example of the invention, a DARC 193  $\text{SiO}_x\text{H}_y$  : C film having an  
20 n of 1.9 and a k of 0.3 @ 248 nm, which was surface treated with a helium plasma  
21 generated using a single frequency power source, for a time period of about 10 to about 30  
22 seconds, using a helium flow rate of 5 slm in the 200 mm PRODUCER® twin PECVD  
23 process chamber, at a pressure of ranging from about 2 Torr to about 10 Torr (typically  
24 about 5.5 Torr), at a substrate temperature of about  $350 \pm 50$  °C, at a plasma source power  
25 of 50 - 100 W at 13.56 MHz, and at a shower head spacing of 450 mils from the substrate  
26 surface, exhibited a contact angle of about 32 degrees to about 40 degrees (for the 10  
27 second and 30 second treatment periods, respectively) with respect to the same developer

1 mentioned above. Exposure of the photoresist CAR to  $230 \text{ J/m}^2$  or  $280 \text{ J/m}^2$  of 248 nm  
2 patterning radiation, followed by development of the image using the developer produced  
3 an acceptable pattern of approximately 110 nm features in the CAR over the substrate  
4 surface as a whole. However, there were some areas on the substrate surface which were  
5 substandard. There is no representative Figure shown which illustrates this example.

6 [0079] Example Six:

7 [0080] In a third example of the invention, a nitrogen-free DARC 193  $\text{SiO}_x\text{H}_y$  : C film  
8 having an n of 1.9 and a k of 0.3 @ 248 nm, which was capped with a 15 Å thick  $\alpha$ -Si  
9 coating applied by discontinuing the  $\text{CO}_2$  reagent feed to the DARC 193 single frequency  
10 plasma deposition process. The  $\alpha$ -silicon deposition time period was about 5 seconds,  
11 using a  $\text{SiH}_4$  flow rate of 10 sccm and helium at a 6 slm flow rate in the 200 mm  
12 PRODUCER® twin PECVD process chamber, at a pressure of ranging from about 2 Torr  
13 to about 10 Torr (typically about 5.5 Torr), at a substrate temperature of about  $350 \pm 50^\circ\text{C}$ ,  
14 at a plasma source power of 50 W at 13.56 MHz, and at a shower head spacing of 500 mils  
15 from the substrate surface, exhibited a contact angle of about 34.5 degrees with respect to  
16 the water-based, basic developer. Exposure of the CAR to either  $230 \text{ J/m}^2$  or  $280 \text{ J/m}^2$  of  
17 193 nm patterning radiation, followed by development of the image, produced a very  
18 acceptable pattern of 90 nm features in the CAR which is illustrated in Figure 2C. Figure  
19 2C is a schematic top view 230 of a photomicrograph of the patterned photoresist. The  
20 DARC 193 surface 232 was properly exposed in the developed areas, leaving the  
21 photoresist 236 present in desired areas of the approximately 110 nm feature size pattern.  
22 Although this example is for an  $\alpha$ -silicon capping film, an  $\alpha$ -carbon capping film is  
23 expected to provide similar results.

24 [0081] Example Seven

25 [0082] Figure 2E illustrates a schematic top view 240 of a nitrogen-free DARC 193  
26  $\text{SiO}_x\text{H}_y$  : C film having an n of 1.9 and a k of 0.8 @ 248 nm. The increased k was  
27 obtained by reducing the carbon content of the film to less than about 2.0 %, and



1 increasing the S-H content of the film during deposition of the film, using the process  
2 parameters described above with respect to a nitrogen-free DARC 193 deposition.  
3 However, the increase in S-H content of the film was inadequate and did not produce a  
4 contact angle which was helpful. The contact angle obtained was 3.5 degrees, and  
5 photoresist detachment was observed during development of the photoresist. Although a  
6 230 J/m<sup>2</sup> exposure during patterning did produce an acceptable, the 280 J/m<sup>2</sup> exposure did  
7 not. The schematic top view 240 of the developed pattern for the 280 J/m<sup>2</sup> exposure,  
8 which is illustrated in Figure 2E, shows that, due to detachment and shifting of the  
9 location of portions of the photoresist 246 during development, the DARC 193 surface  
10 242 did not exhibit the proper pattern.

11 [0083] Figure 3 is a graph 300 illustrating the shelf life of the contact angle for a  
12 DARC 193 film which is contacted with an aqueous, basic developer, where the DARC  
13 193 film surface was treated with a helium plasma to improve the contact angle. After  
14 deposition of the nitrogen-free DARC 193 SiO<sub>x</sub>H<sub>y</sub> : C film, the substrate was stored in air  
15 at room temperature (about 27 °C) under typical clean room conditions. The contact angle  
16 is shown on scale 310, with the days after DARC 193 formation and helium plasma  
17 treatment shown on scale 308. Curve 302 illustrates the change in contact angle for a  
18 DARC 193 film,  $n \approx 1.9$ ,  $k \approx 0.3$  @ 248 nm ( a low k DARC), which was exposed to 10  
19 seconds of helium plasma treatment. Curve 304 illustrates the change in contact angle for  
20 the DARC 193 film which was exposed to 30 seconds of helium plasma treatment. Curve  
21 306 illustrates the change in contact angle for the DARC 193 film which was exposed to  
22 60 seconds of helium plasma treatment. It is a surprising result that the longer treatment  
23 times caused the change in contact angle to be more rapid and that the change resulting  
24 from longer treatment times could be so drastic as to cause the contact angle to fall to

1 about 28 degrees. For example, when the helium plasma treatment time is 60 seconds, the  
2 contact angle drops below 30 degrees within 3 days, while the 10 second treatment  
3 provided a 35 degree contact angle after 6 days.

4 [0084] Figure 4 is a graph 400 illustrating the shelf life of the contact angle for a DARC  
5 193 film,  $n \approx 1.9$ ,  $k \approx 0.3$  @ 248 nm ( a low k DARC), which is contacted with the aqueous,  
6 basic developer, where the DARC 193 film surface was treated with a hydrogen plasma  
7 and then stored in the manner described with reference to Figure 3. The contact angle is  
8 shown on scale 410, with the days after DARC 193 formation and hydrogen plasma  
9 treatment shown on scale 408. Curve 402 illustrates the change in contact angle for the  
10 DARC 193 film which was exposed to 10 seconds of hydrogen plasma treatment. Curve  
11 404 illustrates the change in contact angle for the DARC 193 film which was exposed to  
12 30 seconds of hydrogen plasma treatment. Curve 406 illustrates the change in contact  
13 angle for the DARC 193 film which was exposed to 60 seconds of hydrogen plasma  
14 treatment. In the instance of a hydrogen plasma treatment, the change in contact angle is  
15 relatively small over a six day time period, with a slight increase in the contact angle  
16 toward the end of the six day time period. This may be indicative of a reaction taking  
17 place between the surface of the DARC 193 film and the hydrogen so that the hydrogen  
18 becomes a permanent part of the DARC 192 film surface. This is in contrast with the  
19 DARC 193 film treated with the helium plasma, where helium may be absorbed on the  
20 film surface rather than reacted with the surface, since the surface shows a significant  
21 decrease in contact angle over a time period.

22 [0085] The indication that the helium plasma treatment alters the contact angle of the

1 DARC 193 surface in a temporary manner does not mean that the helium plasma treatment  
2 is not useful; it simply means that the DARC 193 surface must be used within a relatively  
3 short time period.

4 [0086] The other concern in the production of feature sizes of 120 nm or less, and in  
5 particular 90 nm or less, is that there will be photoresist poisoning even though the  
6 photoresist remains attached during development. To have proper pattern formation, it is  
7 necessary that the photoresist remain attached to the substrate during development and that  
8 photoresist poisoning, which will prevent proper pattern development, be avoided. At the  
9 time of development of the nitrogen-free DARC 193, it was anticipated that the absence of  
10 nitrogen would eliminate the poisoning of the acid-based positive CAR, as previously  
11 discussed. However, it was discovered that the presence of -OH radicals on the surface of  
12 the DARC 193 continued to create photoresist poisoning problems. -OH radicals were  
13 suspected to be present due to moisture absorption of the DARC 193 surface.

14 [0087] To avoid photoresist poisoning when the nitrogen-free DARC 193  $\text{SiO}_x\text{H}_y$  :  
15 C film is used, we tried two different approaches. The first approach was to density the  
16 surface of the film so that  $\text{H}_2\text{O}$  absorption would not occur on the film surface. The  
17 second approach was to acidify the film surface to neutralize the effect of  $\text{H}_2\text{O}$  absorption.

18 [0088] We evaluated the differences in reaction with  $\text{O}_2$  plasma and in  $\text{H}_2\text{O}$   
19 absorption on the surfaces of nitrogen-free DARC 193  $\text{SiO}_x\text{H}_y$  : C films of differing  
20 atomic composition, where the films were produced using the single frequency and dual  
21 frequency PECVD deposition techniques described above. The atomic compositions of  
22 the films were adjusted so that  $k = 0.35$ , or  $k = 0.6$ , or  $k = 0.95$ , with  $k$  values being  $\pm 0.05$ .  
23 We also evaluated the effect of using helium as the inert gas in the plasma source gas

1 compared with argon as the inert gas.

2 [0089] The photoresist applied over the nitrogen-free DARC 193 film was TARF-  
3 6A-101, available from TOK company (Tokyo Ohka Kogyo Co. Ltd.) of Kawasaki, Japan,  
4 a 193 nm radiation exposure CAR. The patterning of this film was carried out using a  
5 CANON® AS 2 radiation source. The pattern was developed using an aqueous, basic  
6 developer supplied by TOK company for use with the TARF-6A-101 photoresist.

7 [0090] Figure 5 is a graph showing compressive stress in Mpa on scale 504, for a  
8 nitrogen-free DARC 193  $\text{SiO}_x\text{H}_y$  : C film of varying atomic composition (which provides  
9 a  $k = 0.35$ ,  $k = 0.6$ , or  $k = 0.95$ , as a function of process conditions indicated on the 502  
10 scale. SF represents a single frequency PECVD deposition of the DARC 193 film, while  
11 MF indicates a multiple (dual) frequency PECVD deposition of the DARC 193 film. Ar  
12 represents the use of argon as the inert gas in the plasma source gas, while He indicates  
13 helium as the inert gas in the plasma source gas. The compressive stress for each film  
14 composition is shown to increase when MF frequency deposition is used and when helium  
15 is used as the inert gas. In addition, when the power input to the plasma is reduced, so that  
16 the film is deposited more slowly, it is possible to get a significant increase in compressive  
17 stress of the film. Curve 506 represents a nitrogen-free DARC 193 film having an initial  
18 extinction coefficient of 0.35; Curve 508 represents the DARC 193 film having an initial  
19 extinction coefficient of 0.6; and Curve 510 represents the DARC 193 film having an  
20 initial extinction coefficient of 0.95. A higher compressive stress of the film has been  
21 correlated to a more dense film, as described below.

22 [0091] Figure 6 is a graph 600 which shows the reduction in extinction coefficient on  
23 scale 604 for the nitrogen-free DARC 193 film subsequent to  $\text{O}_2$  plasma ashing for

1 photoresist removal, as a function of process conditions specified on scale 602. Again, SF  
2 represents single frequency plasma deposition of the film, while MF indicates multiple  
3 frequency deposition. Ar represents the use of argon as the inert gas in the plasma source  
4 gas, while He represents the use of helium. A review of Figure 6 clearly indicates that the  
5 extinction coefficient  $k$  of the nitrogen-free DARC 193 film experiences less of a  
6 reduction after the  $O_2$  ashing when multiple frequency PECVD deposition of the film is  
7 carried out, when helium is used as the inert gas in the plasma source gas, and when the  
8 film deposition rate is slower. Curve 606 represents the DARC 193 film having an initial  
9 extinction coefficient of 0.35; Curve 608 represents the film having an initial extinction  
10 coefficient of 0.6, and Curve 610 represents the film having an initial extinction  
11 coefficient of 0.95. The slower reduction in extinction coefficient which occurs upon  $O_2$   
12 ashing clearly correlates with the increase in compressive strength of the film which is  
13 illustrated in Figure 5.

14 [0092] Figure 7 is a graph 700 which shows the reduction in extinction coefficient on  
15 scale 704 for the nitrogen-free DARC 193 film after 9 days of standing a room temperature  
16 in a clean room ambient, as a function of process conditions specified on scale 702.  
17 Again, SF represents single frequency plasma deposition of the film, while MF indicates  
18 multiple frequency deposition. Ar represents the use of argon as the inert gas in the plasma  
19 source gas, while He represents the use of helium. Curve 706 represents the DARC 193  
20 film having an initial extinction coefficient of 0.35, Curve 708 represents the film having  
21 an initial extinction coefficient of 0.6, and Curve 710 represents the film having an initial  
22 extinction coefficient of 0.95. A review of Figure 7 clearly indicates that the extinction  
23 coefficient  $k$  of the nitrogen-free DARC 193 film experiences less of a reduction after

1 standing in the clean room when multiple frequency PECVD deposition of the film is  
2 carried out, when helium is used as the inert gas in the plasma source gas, and when the  
3 film deposition rate is slower. Although the correlation is not as good as for O<sub>2</sub> ashing,  
4 clearly the shelf life of the extinction coefficient for the nitrogen-free DARC 193 film also  
5 correlates with the increase in compressive strength of the film which is illustrated in  
6 Figure 5.

7 [0093] Figure 8 is a graph 800 which shows the reduction in refractive index  $n$  on  
8 scale 802 for the nitrogen-free DARC 193 film as a function of the compressive stress of  
9 the film indicated on scale 804. Curve 806 represents the DARC 193 film having an initial  
10 extinction coefficient of 0.35, Curve 808 represents the film having an initial extinction  
11 coefficient of 0.6, and Curve 810 represents the film having an initial extinction coefficient  
12 of 0.95. Figure 8 shows that a nitrogen-free DARC 193 film having a higher compressive  
13 strength initially will provide a smaller change in refractive index after O<sub>2</sub> ashing. Figure 8  
14 also shows that a nitrogen-free DARC 193 film having a higher extinction coefficient  
15 initially (due to atomic composition) is subject to a greater proportional reduction  
16 in magnitude after O<sub>2</sub> ashing as the initial compressive stress of the film decreases.

17 [0094] Figure 9 is a graph 900 which shows the reduction in extinction coefficient  $k$   
18 on scale 902 for the nitrogen-free DARC 193 film as a function of the compressive stress  
19 of the film indicated on scale 904. Curve 906 represents the DARC 193 film having an  
20 initial extinction coefficient of 0.35, Curve 908 represents the film having an initial  
21 extinction coefficient of 0.6, and Curve 910 represents the film having an initial extinction  
22 coefficient of 0.95. Figure 9 shows that a nitrogen-free DARC 193 film having a higher

1 compressive strength initially will provide a smaller change in extinction coefficient after  
2 O<sub>2</sub> ashing.

3 [0095] According to Fourier Transform Infrared Spectroscopy (FTIR) data with  
4 respect to the presence of an -OH absorption peak, a nitrogen-free DARC 193 film  
5 produced using single frequency PECVD which exhibits a lower compressive stress is  
6 more susceptible to moisture absorption.

7 [0096] No -OH absorption peak was observed for nitrogen-free DARC 193 films  
8 produced using multiple frequency PECVD. This suggests that the use of multiple  
9 frequency power input during film deposition produces a higher compressive stress film  
10 which is resistant to H<sub>2</sub>O absorption. As a result, photoresist poisoning will be reduced  
11 when DARC 193 films are produced using multiple frequency PECVD.

12 [0097] Cross-sectional scanning electron microscope images for photoresists  
13 patterned to approximately 90 nm feature sizes (in a lines and spaces pattern) have  
14 indicated that footing at the bottom of the photoresist after development is substantially  
15 reduced when the nitrogen-free DARC 193 film underlies the photoresist, compared with a  
16 prior art nitrogen-containing DARC film. The amount of footing is further reduced when  
17 multiple frequency PECVD deposition of the DARC 193 film is used rather than single  
18 frequency PECVD deposition. Use of helium as the inert gas in the multiple frequency  
19 PECVD deposition of the film reduces the footing even more. Finally, the least footing  
20 observed when a slower deposition rate for the film is combined with the multiple  
21 frequency/helium PECVD deposition.

22 [0098] The above described exemplary embodiments are not intended to limit the  
23 scope of the present invention, as one skilled in the art can, in view of the present

- 1 disclosure expand such embodiments to correspond with the subject matter of the
- 2 invention claimed below.